CHEMISTRY LETTERS, pp. 269-272, 1991.

Reactions of Meso-ionic Compounds with Metal Complexes. Formation of (η^5-Cyclopentadienyl)(1,2-diaryl-1,2-ethylenedithiolato)-cobalt(III) Complexes in the Thermal and Photochemical Reactions of 2,5-Diaryl-1,3-dithiolylium-4-olate with [Co(cp)] Species

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The title meso-ionic compounds react thermally and photochemically with [Co(cp)] species to give dithiolatocobalt complexes. 5-Phenyl-2-(p-tolyl)-1,3-dithiolylium-4-olate gives (η^5-cyclopentadieny)(1-phenyl-2-(p-tolyl)-1,2-ethylenedithiolato)cobalt(III) with high selectivity.

We can expect unique reactions between highly polar meso-ionic compounds and transition metal complexes. However, very few studies have been done on such systems. One example is the reaction between 2,3-diphenyl-1,2,3,4-tetrazolylium-5-thiolate and pentacarbonyliron.[1] However, even in that case, the interest was focused on the reactions of organic compound and there was no description on the organometallic products. Recently, Kalinin et al. reported the coupling of sydnone with iron and nickel complexes.[2,3]

We report here the formation of the dithiolatocobalt complexes ((η^5-cyclopentadienyl)(1,2-diaryl-1,2-ethylenedithiolato)cobalt(III): **3**) in the thermal and photochemical reactions of meso-ionic 2,5-diaryl-1,3-dithiolylium-4-olates (**1a**: 2,5-diphenyl, **1b**: 5-phenyl-2-(p-tolyl)) with [Co(cp)(cod)] (**2a**: cod=1,5-cyclooctadiene) or [Co(cp)(CO)$_2$] (**2b**).

On all thermal reactions described below, a mixture of **1** and **2** was refluxed in xylene at 140 °C under Ar, while on photoreactions, a benzene solution of **1** and **2** was irradiated with a medium pressure mercury lamp at room temperature under Ar. Under both thermal and photochemical reactions between **1a** and **2**, (η^5-cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III) complex (3a) was obtained in considerable yields.

In order to determine the origin of the aryl groups incoporated in the dithiolato complex, 5-phenyl-2-(p-tolyl)-1,3-dithiolylium-4-olate (1b) was used as a substrate. In the thermal and photochemical reactions of 1b with carbonyl complex 2b, the dithiolato complex carrying both p-tolyl and phenyl groups (3b) was formed selectively. In the thermal reaction of 1b with cyclooctadiene complex 2a, together with 3b the dithiolato complexes carrying two phenyl groups 3a and carrying two p-tolyl groups 3c were obtained as byproducts. The photoreaction of 1b and 2a gives 3b selectively. The results obtained from thermal and photochemical reactions are summarized in Table 1.

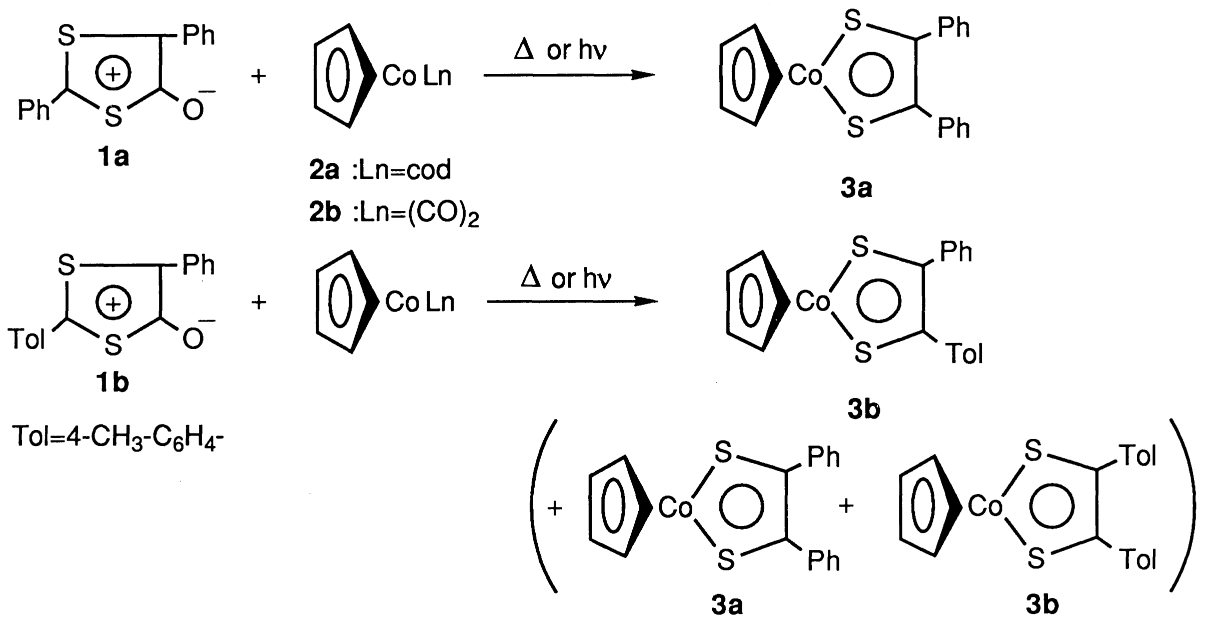


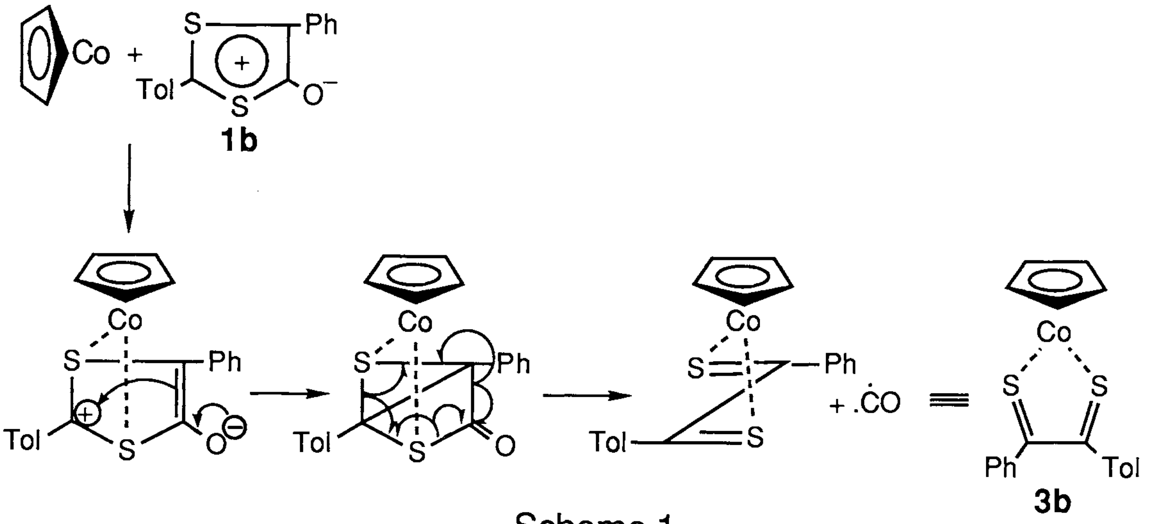
Table 1. Thermal and photochemical reactions between 2,4-diaryl-1,3-dithiolylium-5-olate (1) and [Co(cp)L_n] (2)

Meso-ion 1	Amount μmol	Metal complex 2	Amount μmol	Reaction conditions	Yield of complex 3 % 3a	3b	3c
1a	300	2a	150	Δ $^{a)}$ 140 °C, 24 h	35	--	--
1a	350	2b	180	Δ $^{a)}$ 140 °C, 3 h	43	--	--
1a	50	2a	25	hν $^{b)}$ 20 h	55	--	--
1b	300	2a	150	Δ $^{a)}$ 140 °C, 24 h	2.8	14	4.2
1b	356	2b	178	Δ $^{a)}$ 140 °C, 5 h	0	64	trace
1b	50	2a	25	hν $^{b)}$ 30 h	0	32	0

a) Reflux in xylene. b) Irradiation with a medium pressure mercury lamp.

The heating of 1b in xylene in the absence of 2a causes no reaction of 1b. The presence of 2a brings about the rapid disappearance of 1b. The rate of disappearance of 1b increases with the increase in the concentration of 2a. This fact suggests that the coordinatively unsaturated [Co(cp)] species attacks the meso-ionic compound. During the thermal reaction, the evolution of CO was observed. In the thermal reaction of 1b and 2a under the conditions described in the 4th row in Table 1, ca 10 μmol of CO were detected.

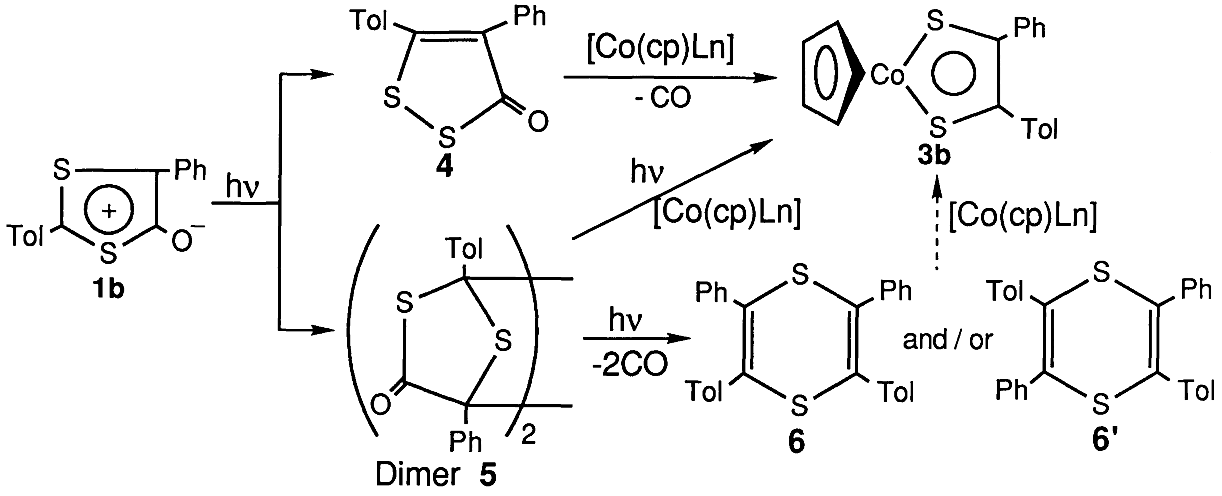
Thus, we can postulate a possible mechanism in Scheme 1 for the formation of the main product 3b.



Scheme 1.

After irradiation of 1b in benzene, the cobalt complex 2 was added to the reaction mixture, and this gave 3b selectively. Kato et al. have reported that the irradiation of 1a gives a dimer, tetraphenyl-1,4-dithiin, 4,5-diphenyl-1,2-dithiol-3-one, diphenylacetylene, and elemental sulphur.[4] Among the photoproducts from 1b, 5-phenyl-4-(p-tolyl)-1,2-dithiol-3-one (4) reacted with 2b to give selectively 3b. The dimer (5) did not react with 2b in the dark, but reacted under irradiation to give 3b selectively. The 1,4-dithiin, which was reported to be formed in the photoreaction of 5, may react with 2 to give the dithiolatocobalt complex.[5] However, the 1,4-dithiins with low electron-accepting substituents (such as phenyl) have low reactivities. The path via 1,4-dithiin and [Co(cp)L_n] may exist, but with small contribution.

The above facts indicate that the dithiolatocobalt complexes are formed in the reactions between [Co(cp)] species and several photoproducts from 1 (Scheme 2).



Scheme 2.

The authors are very grateful to Professor Hiroshi Kato of Shinshu University for sending the specimen of photoproducts of the meso-ionic compound and for helpful discussions. The present work was partially supported by Grant-in-Aid for Scientific Research on Priority Areas on Organic Unusual Valency No. 02247102 and by Grant-in-Aid for Scientific Research, Science and Culture No. 02640406 from the Ministry of Education, Japan, and by financial aid from Asahi Glass Foundation.

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(Received October 31, 1990)